



Development of ammonia sensors by using conductive polymer/hydroxyapatite composite materials



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ABSTRACT

In order to improve the gas sensing properties, hydroxyapatite (HAp)-based composites were prepared by mixing with different contents of conductive polymers: polypyrrole (PPy) and polyaniline (PAni). The compositions, microstructures and phase constitutions of polymer/HAp composites were characterized, and the sensing properties were studied using a chemical gas sensing (CGS-8) system. The results showed that, compared to pure HAp, the sensitivities of the composites to ammonia were improved significantly. 5%PPy/HAp and 20%PAni/HAp composites exhibited the best sensitivities to ammonia, and the sensitivities at 500 ppm were 86.72% and 86.18%, respectively. Besides, the sensitivity of 5%PPy/HAp at 1000 ppm was up to 90.7%. Compared to pure PPy and PAni, the response and the recovery time of 5%PPy/HAp and 20%PAni/HAp at 200 ppm were shortened several times, and they were 24 s/245 s and 15 s/54 s, respectively. In addition, the composites showed a very high selectivity to ammonia. The mechanism for the enhancement of the sensitivity to ammonia was also discussed. The polymer/HAp composites are very promising in applications of ammonia sensors.

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1. Introduction

Ammonia, a poisonous gas with a pungent stench, can endanger the health and safety of human body after an excessive inhalation. The smell detection limit of human body to ammonia is about 50 ppm, and it may take about 24 h before the unpleasant symptoms develop. Therefore, the detection of ammonia in a trace level is important since the leakage of ammonia in chemical industry, vehicle and combustion systems has become an un-negligible problem. The Occupational Safety and Health Administration (OSHA) has set an acceptable limit of 25 ppm of ammonia at an exposure of 8 h and a short-term (15 min) exposure level of 35 ppm for human beings at the workplace [1,2]. Inorganic metal oxide semiconductors, like ZnO [3], TiO₂ [4], WO₃, Cr₂O₃ and In₂O₃ [5], have been applied as sensor materials for ammonia, but their operation temperatures are often above 300 °C. Even though some composite films are developed to measure ammonia at room temperature, the sensitivity is relatively low and the lack of selectivity is still a difficult problem to handle [6].

Since iodine-doped polyacetylene with high conductivity was found by Shirakawa in 1977, conductive polymers including polyaniline (PAni), polypyrrole (PPy) and polythiophene (PT) et al. have been extensively explored recent years due to their excellent chemical and physical properties originating from their unique π -conjugated system.

They are easy to be synthesized and processed, and have high electrical conductivity and long term environmental stability, which make them useful in electronic, optoelectronic and electromechanical field. One of the most popular applications is sensors. For example, conductive polymers have been used to fabricate composites biosensors with CNTs [7,8] and Fe₃O₄ [9,10] for the detection of H₂O₂ [11] and glucose [12], which exhibit high sensitivity and low detection limit. PPy [13] and PAni [14] are the most frequently used and studied polymers for sensing ammonia, the sensing properties can be measured at room temperature. However, the sensitivity and the selectivity of PPy and PAni to ammonia prepared by chemical oxidative polymerization are lower than those prepared by the electrochemical deposition, and the response time and the recovery time are very long. Besides, the irreversibility and the insolubility are serious problems remained to be solved [15,16]. To combine the properties of pure organic and inorganic materials for gas sensor applications, composite materials such as PPy/WO₃ [17], PPy/SnO₂ [18,19], PPy/ZnO [20], PPy/Fe₂O₃ [21], PPy/MoO₃ [22], PPy/NiO [23] PAni/SnO₂ [24,25] and PAni/TiO₂ [26–31] have been developed to improve the gas sensing properties to H₂S, NH₃ and NO₂. Although the sensitivity, reversibility and response/recovery time for ammonia are improved compared to pure PPy and PAni, the recovery time of the composites is still as long as hundreds of seconds. Besides, the sensitivities of the sensing materials can barely reach 90% and there is still about 10% of shift of the initial value after several cycles of measurement.

In our previous work, the tubular hydroxyapatite (HAp) prepared by an electrochemical deposition method assisted with a cation exchange membrane showed excellent sensing properties to ammonia, and the sensing mechanisms to ammonia were proposed [32]. In this paper,

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PPy and PANi were used to be mixed with tubular HAp to further enhance the sensing properties to ammonia. The sensitivity, response/recovery time, selectivity of pure PPy, PANi, HAp, PPy/HAp composites and PANi/HAp composites to ammonia were studied. Besides, the sensing mechanisms of the polymer/HAp composites to ammonia were discussed.

2. Materials and methods

The Nafion N-117 cation-exchange membrane, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were purchased from Alfa Aesar. All other chemicals (such as $\text{NH}_3 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{S}_2\text{O}_8$, HCl and N,N'-dimethyl formamide (DMF)) were of analytical reagent grade, and used as received unless otherwise noted. Pyrrole (Py) and aniline (Ani) were distilled under reduced pressure, put in a desiccator and stored in the refrigerator (0–4 °C). Deionized water (DI water) was produced by ULUP-1–20 T.

PPy and PANi were prepared by a chemical oxidative polymerization method at room temperature. The volume ratios of pyrrole and aniline monomers to the oxidant of $\text{NH}_4\text{S}_2\text{O}_8$ were 1:1, respectively. 1 mol/L HCl was used to add H^+ to PPy and PANi. The tubular HAp was fabricated using an electrochemical deposition method assisted with a cation exchange membrane, followed by stewing at 50 °C for 7 days [32–34]. The microstructures and compositions of the samples were characterized by Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) analyses, respectively.

Organic–inorganic composite materials of PPy/HAp and PANi/HAp were prepared by mechanically mixing. PPy, PANi and HAp were dispersed in N,N'-dimethyl formamide (DMF), respectively, and the HAp suspension was added into the PPy and PANi suspensions dropwise, then the mixed suspension was stirred continuously for 24 h at room temperature. According to the different mass content of polymer, the obtained composites were described as 2.5%PPy/HAp, 5%PPy/HAp, 10%PPy/HAp, 1%PANi/HAp, 5%PANi/HAp, 10%PANi/HAp, 20%PANi/HAp, 30%PANi/HAp and 50%PANi/HAp, respectively.

Gas sensing properties were measured by a CGS-8 (Chemical gas sensor-8) intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd., China). In the gas-sensing tests, ammonia was selected as the major target gas at room temperature. PPy, PANi, HAp, PPy/HAp and PANi/HAp composites were coated on a ceramic tube with 4 Au electrodes. A Ni–Cr alloy wire was used as a heating filament across the tube. All the gas sensing properties were measured in a 1 dm³ glass bottle. Firstly, the bottle was vacuumed, and injected with a certain amount of ammonia. After the ammonia diffused absolutely in the bottle, the air

was allowed to enter and mix homogeneously. Secondly, the gas sensor was put into the bottle immediately, and the electric resistance of the sensor changed rapidly. When the resistance reached a stable level, the sensor was taken out, and the resistance came back to the initial value. The sensitivity was defined as $S = (\text{Ra} - \text{Rg}) / \text{Ra} * 100\%$, where Ra and Rg were the resistances of the sensor in ambient air and target gas, respectively. The response time and the recovery time of the sensor were the time required for a change in the resistance of the sensor to reach 90% of the equilibrium value after injecting and removing the target gases, respectively. The resistance of the sensor was measured according to the schematic diagram, as shown in Fig. 1. The working temperature of the sensor could be controlled by adjusting the heating current across the resistor inside the ceramic tube. Since the sensing properties of the sensors in the experiments were measured at room temperature, the current value was zero. Reference resistors which could automatically select were put in series with the sensor to form a complete measuring circuit. According to the working voltage and the resistance of the reference resistors, we knew the current of the measuring circuit. Then the resistance of the sensor could be calculated.

3. Results and discussions

Fig. 2 shows the XRD patterns of PPy, PANi, HAp, 10%PPy/HAp, 50%PANi/HAp composite. Pure PPy has a broad, amorphous diffraction peak centered at about $2\theta = 26^\circ$. PANi exhibits a certain degree of crystallinity, and shows similar strong peaks at $2\theta = 20.44^\circ$ and 25.1° , corresponding to (100) and (110) planes, respectively. For HAp, all the diffraction peaks can be indexed as a pure hexagonal phase with a space group of P63/m, in consistence with the standard patterns of HAp (PDF 09-0432). The sharp peak at $2\theta = 25.9^\circ$ indicates a good crystallization and growth preference on the (002) crystal plane. In addition, the HAp has a crystallinity of 86.87% according to the calculation. However, the peaks of PPy and PANi cannot be seen obviously in the XRD patterns of the composites. It may be because the diffraction peaks of PPy and PANi are weak and covered by the background of the HAp peaks.

Fig. 3 shows the SEM images of HAp (a), PPy (b), PANi (c), PPy/HAp composite (g), PANi/HAp composite (j) and TEM images of HAp (d), PPy (e), PANi (f), PPy/HAp composite (h), PANi/HAp composite (i). HAp shows a tubular structure with a diameter of 2.5–5 μm , and a length of 5–20 μm (Fig. 3(a)). In the TEM image, it can be seen that the tubular HAp consists of nanorods (Fig. 3(d)). HAp nanorods aggregate in a certain orientation to form clusters and then form tubular HAp after a process of self-assembly with the assist of cation-exchange membrane. PPy exhibits a uniform spherical morphology (Fig. 3(b)). The diameter

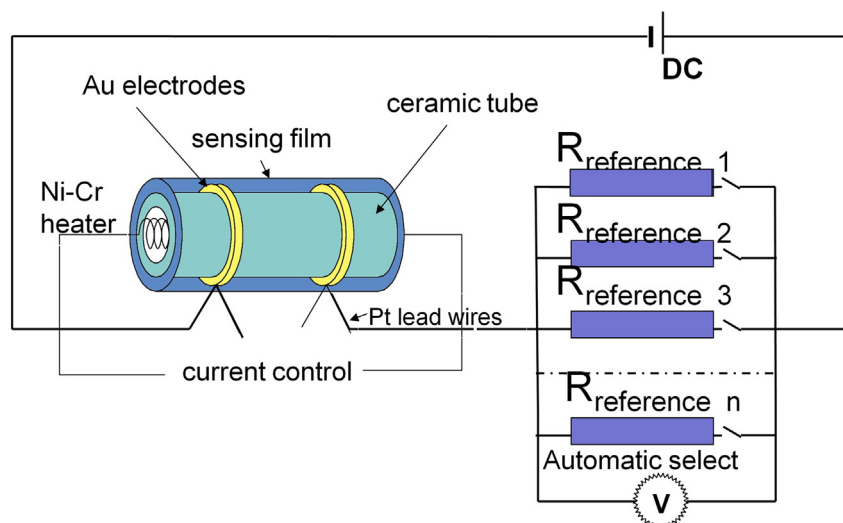


Fig. 1. Schematic diagram of the resistance measurement of sensors.

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